

**The Determination of Accurate Dipole Polarizabilities  
 $\alpha$  and  $\gamma$  for the Noble Gases**

Julia E. Rice

IBM Research Division, Almaden Research Center  
650 Harry Rd., San Jose, CA 95120-6099

Peter R. Taylor<sup>†</sup>  
ELORET Institute  
Palo Alto, CA 94303

Timothy J. Lee  
NASA Ames Research Center  
Moffett Field, CA 94035

and

Jan Almlöf  
Department of Chemistry and Minnesota Supercomputer Institute  
University of Minnesota, Minneapolis, MN 55455

**Abstract**

The static dipole polarizabilities  $\alpha$  and  $\gamma$  for the noble gases helium through xenon have been determined using large flexible one-particle basis sets in conjunction with high-level treatments of electron correlation. The electron correlation methods include single and double excitation coupled-cluster theory (CCSD), an extension of CCSD that includes a perturbational estimate of connected triple excitations, CCSD(T), and second-order perturbation theory (MP2). The computed  $\alpha$  and  $\gamma$  values are estimated to be accurate to within a few percent. Agreement with experimental data for the static hyperpolarizability  $\gamma$  is good for neon and xenon, but for argon and krypton the differences are larger than

<sup>†</sup> Mailing address: NASA Ames Research Center, Moffett Field, California 94035-1000

NCC 2-371  
IN-25-CT  
85228  
p 25

the combined theoretical and experimental uncertainties. Based on our calculations, we suggest that the experimental value of  $\gamma$  for argon is too low: adjusting this value would also bring the experimental value of  $\gamma$  for krypton into better agreement with our computed result. The MP2 values for the polarizabilities of neon, argon, krypton and xenon are in reasonable agreement with the CCSD and CCSD(T) values, suggesting that this less expensive method may be useful in studies of polarizabilities for larger systems.

## 1. Introduction

There is considerable interest in the non-linear polarizabilities of atoms and molecules. An understanding of these higher-order electrical properties is particularly important for the field of non-linear optics. The first hyperpolarizability  $\beta$  is related to the electro-optic effect and second harmonic generation, and the second hyperpolarizability  $\gamma$  is related to third (and second) harmonic generation and the Kerr effect. These non-linear processes have applications in areas such as optical disk storage and optical switches.

There are three main factors to be considered in the *ab initio* calculation of hyperpolarizabilities, and the subsequent comparison of theoretical and experimental results. First, an accurate description of the response of the electron density to an applied electric field is required, which necessitates the use of large one-particle basis sets and an accurate treatment of electron correlation. Second, experimental investigations of these properties involve frequency-dependent electric fields, so if a direct comparison with experiment is to be made the frequency dependence must be computed explicitly. Third, for molecules a vibrational dependence, which in some cases may be large,<sup>1</sup> should also be evaluated. It is evidently useful to obtain an understanding of atomic hyperpolarizabilities, since one of these factors, the vibrational contribution, is eliminated. In addition, in some cases it should be possible to avoid computing the frequency dependence, since an extrapolation of the experimental hyperpolarizability  $\gamma$  to zero frequency is possible, as has been demonstrated for the noble-gas atoms, for example.<sup>2</sup>

A study of the noble-gas atoms can provide insight into the requirements for an accurate theoretical determination of static second hyperpolarizabilities. The wave functions of the noble gases are strongly dominated by the Hartree-Fock configuration, and thus highly accurate correlation treatments may be employed at relatively modest computational expense. In our initial study on  $\gamma$  for neon,<sup>3</sup> it was demonstrated that quantitative accuracy could be achieved using a single and double excitation coupled-cluster wave function with a perturbational estimate of connected triple excitations,<sup>4</sup> denoted CCSD(T), in conjunction with an augmented atomic natural orbital<sup>5</sup> (ANO) basis set including up to three diffuse *f* functions. In the present study,  $\gamma$  is determined for the noble gases helium through xenon, using wave functions of similar quality for each system. The theoretical results are accurate enough to allow an assessment of the experimental static values ob-

tained from extrapolation to zero frequency. Finally, we consider the accuracy attainable with more approximate methods, in particular second-order Møller-Plesset perturbation theory, a method which is tractable for large systems since it is much less expensive than e.g. CCSD(T).

Our computational approach is outlined in the following section, while the polarizabilities of argon, krypton and xenon are discussed in section 3. In order to facilitate comparisons involving the entire series of noble-gas atoms, values for helium, obtained using the same methods, and our previous values for neon<sup>3</sup> are also summarized in section 3. Our conclusions are presented in section 4.

## 2. Computational Approach

The polarizabilities  $\alpha$  and  $\gamma$  are defined, following Buckingham,<sup>6</sup> by the equation

$$E(F) = E_0 - \frac{1}{2}\alpha F^2 - \frac{1}{24}\gamma F^4 \dots$$

for the energy of an atom in an  $S$  state, subjected to an applied homogeneous static electric field of strength  $F$ .

We will first outline the general design of the one-particle basis sets used in this study, and then describe in detail the sets used. For each atom, a Gaussian primitive set was chosen and contracted using atomic natural orbitals (ANOs)<sup>5</sup>, e.g.  $[4s\ 3p\ 2d]$  for helium. One or more of the outermost primitive functions were then “uncontracted”, that is, included as independent basis functions in the final basis: this is denoted  $[4+1+1s\ 3+1+1p\ 2+1d]$  when e.g. the outermost two  $s$ , two  $p$  and one  $d$  primitive are uncontracted. Additional diffuse functions were then added by extrapolating the orbital exponents from the most diffuse function in an even-tempered sequence,  $\zeta = 2.5^{-n}\zeta_0$ . A supplementary basis including one diffuse function each of  $spd$  type is denoted  $+(1s\ 1p\ 1d)$ . Further higher angular momentum functions were also included in some basis sets, as described below. Only the spherical harmonic components of the basis sets were used.

### Helium

The primitive Gaussian basis set for helium was derived from van Duijneveldt’s  $(10s)$  set<sup>7</sup>, augmented with a  $(6p\ 4d)$  polarization set. The exponents were chosen as an even-tempered sequence  $\zeta = 2.5^{-n}\zeta_0$ ;  $n = 0, \dots, k$  with the largest exponents  $\zeta_0 = 9.88, 4.74$  for the  $p$  and  $d$  functions, respectively. This set was contracted to  $[4s\ 3p\ 2d]$ .

The outermost functions were uncontracted and diffuse functions were added giving a  $[4+1+1s\ 3+1+1p\ 2+1d] + (3s\ 2p\ 2d)$  basis.

In order to determine the effect of higher angular momentum functions a larger primitive basis was used, including a  $(3f)$  set. The  $f$  set was based on an even-tempered sequence with  $\zeta_0 = 3.60$  and a ratio of  $(2.5)^{-1}$  between successive exponents. This primitive basis was contracted to  $[4s\ 3p\ 2d\ 1f]$ . The outermost functions were uncontracted and diffuse functions were added giving a  $[4+1+1s\ 3+1+1p\ 2+1d\ 1+1f] + (3s\ 2p\ 2d\ 2f)$  basis.

### Neon

Full details of the basis sets used for neon are given in Ref 3. These sets were derived from a  $[4s\ 3p\ 2d\ 1f]$  ANO basis by uncontracting the outermost primitives and adding diffuse functions. In the calculations where core correlation was included, the primitive set was augmented with two tighter  $d$  functions (exponents 123.53 and 49.41) in addition to the appropriate diffuse functions.

### Argon

The primitive Gaussian basis set was derived from Partridge's  $(17s\ 12p)$  set<sup>8</sup> augmented with a  $(6d\ 4f)$  polarization set, with exponents chosen as an even-tempered sequence  $\zeta = 2.5^{-n}\zeta_0$ ;  $n = 0, \dots, k$  with  $\zeta_0 = 6.88$  and  $3.30$  for the  $d$  and  $f$  functions, respectively. This was contracted to  $[5s\ 4p\ 2d\ 1f]$  using ANOs. The outermost functions were uncontracted and diffuse functions were added giving a  $[5+1+1s\ 4+1+1p\ 2+1+1d\ 1+1f] + (3s\ 3p\ 3d\ 3f)$  basis. The effect of diffuse higher angular momentum functions was investigated by including two  $g$  functions with exponents of  $0.102$  and  $0.0408$ . Core correlation effects were considered using an  $[11s\ 9p]$  contraction of the  $(17s\ 12p)$  primitive set with the uncontracted  $(6d\ 4f)$  primitive set and with two additional  $d$  functions with exponents  $42.99$  and  $17.20$ .

### Krypton

The primitive Gaussian basis set was derived from Partridge's  $(21s\ 16p\ 10d)$  set<sup>9</sup> augmented with a  $(4f)$  polarization set, with exponents chosen as an even-tempered sequence  $\zeta = 2.5^{-n}\zeta_0$ ;  $n = 0, \dots, k$  with  $\zeta_0 = 2.57$  and with two additional  $d$  functions, obtained by extrapolating from the outermost  $d$  function, with  $\zeta_d = 0.229, 0.0916$ . This primitive set was contracted to  $[6s\ 5p\ 3d\ 1f]$ . The outermost functions were uncontracted and diffuse functions were added giving a  $[6+1+1s\ 5+1+1p\ 3+1+1d\ 1+1f] + (3s\ 3p\ 3d\ 3f)$

basis. The effect of diffuse higher angular momentum functions was investigated by including three  $g$  functions with exponents of 0.0768, 0.0307, and 0.0123. Core correlation effects were considered using a basis constructed from the  $[6s\ 5p\ 3d\ 1f]$  basis by uncontracting the innermost  $f$  function and adding an  $f$  function with  $\zeta_f=6.425$ . This basis, with diffuse extensions, is denoted  $[6+1+1s\ 5+1+1p\ 3+1+1d\ 3+1f] + (3s\ 3p\ 3d\ 3f)$ . The addition of another  $f$  function,  $\zeta_f=16.0625$ , was also investigated.

## Xenon

The primitive Gaussian basis set was derived from Partridge's (24s 19p 13d) set<sup>10</sup> augmented with a (4f) polarization set, with exponents chosen as an even-tempered sequence  $\zeta = 2.5^{-n}\zeta_0$ ;  $n = 0, \dots, k$  with  $\zeta_0 = 1.78$  and with two additional  $d$  functions,  $\zeta_d = 0.1504$  and  $0.0602$ , obtained by extrapolating from the outermost  $d$  function. This was contracted to  $[7s\ 6p\ 4d\ 1f]$ . The outermost functions were uncontracted and diffuse functions were added giving the  $[7+1+1s\ 6+1+1p\ 4+1+1d\ 1+1f] + (3s\ 3p\ 3d\ 3f)$  basis. The effect of diffuse higher angular momentum functions was investigated by including three  $g$  functions with exponents of 0.0547, 0.0219, and 0.0088. Core correlation effects were considered using a basis constructed from the  $[7s\ 6p\ 4d\ 1f]$  basis by uncontracting the innermost  $f$  function and adding two  $f$  functions with exponents  $\zeta_f=4.45$  and  $11.125$ . This basis with diffuse extensions is denoted  $[7+1+1s\ 6+1+1p\ 4+1+1d\ 4+1f] + (3s\ 3p\ 3d\ 3f)$ .

Self-consistent field (SCF), second-order Møller-Plesset (MP2) perturbation theory, and single and double excitation coupled-cluster (CCSD) methods were used. The SCF wave functions were converged to  $10^{-11}$  or better and the CCSD wave function to  $10^{-10}$ . The effect of connected triple excitations was explored using the CCSD(T) method,<sup>4</sup> which includes a perturbational estimate of connected triple excitations based on the converged CCSD amplitudes. From comparison with benchmark calculations on neon,<sup>3</sup> the CCSD(T) method is expected to give valence correlation energies very close to those from a full CI wave function. Calculations were also performed in which the outermost shell of core electrons were correlated (the  $L$  shell for argon,  $M$  shell for krypton, etc). In order to provide a reliable estimate of core correlation effects, the basis sets had to be extended considerably. Because of the computational expense when up to 26 electrons are correlated, the core correlation calculations were performed at the MP2 level, al-

though this approach was calibrated against the CCSD method for argon. The difficulty of computing accurate core correlation contributions is probably the greatest source of uncertainty in our values, as will be discussed further in the next section.

An estimate of the relativistic correction to  $\gamma$  for krypton and xenon at the SCF level of theory was obtained from first-order perturbation theory, defining the relativistic contribution to the energy as an expectation value of the wave function over the mass-velocity and Darwin operators<sup>11</sup> for each field strength.

A variety of electric fields in the range 0 to 0.020 a.u. were used and the total energies obtained were fitted to a polynomial in the field strength, containing higher than fourth-order terms. A comparison at the SCF level of  $\gamma$  values obtained from the energy fit with those obtained from first derivatives of  $\beta$  values (obtained as analytic third derivatives) suggests an error in  $\gamma$  due to fitting of no more than 0.5%. In view of this fitting uncertainty we quote krypton and xenon hyperpolarizabilities to three figures only.

The calculations were performed using the MOLECULE-SWEDEN<sup>12</sup>, CADPAC<sup>13</sup> and VCCSD<sup>14</sup> programs, on the NASA Ames Central Computing Facility CRAY Y-MP/832, the NAS Facility Y-MP/8128, and the IBM Almaden Research Center IBM 3090E.

### 3. Results and Discussion

#### A. Argon

Table 1 displays our computed results for the polarizabilities of argon. The Hartree-Fock value for  $\alpha$  converges on 10.76 a.u., in complete agreement with the numerical Hartree-Fock value of 10.76 a.u. of McEachran et al.<sup>15</sup> and with the value of Sitter and Hurst<sup>16</sup>(10.76 a.u.). The SCF value of  $\gamma$  is 967 a.u. in the  $[5+1+1s\ 4+1+1p\ 2+1+1d\ 1+1f] + (3s\ 3p\ 2d\ 3f)$  basis set, and shows little change with the addition of  $g$  functions or further uncontraction of the ANO basis set. This value should be close to the Hartree-Fock limit; it can be compared with previous results of 1010 a.u.<sup>16</sup> and 991 a.u.<sup>17</sup> from studies in which convergence with respect to saturation of the one-particle basis set was not extensively investigated.

Both  $\alpha$  and  $\gamma$  increase due to electron correlation, although the relative change is much larger for  $\gamma$  (22%). As with our earlier study of neon,<sup>3</sup> the angular momentum level requirements of the one-particle basis set can be determined at the SCF level of theory. Diffuse  $g$  functions hardly affect  $\alpha$  or  $\gamma$  at correlated levels of theory, while of course they cannot contribute at all at the SCF level in the limit of an infinitesimal perturbation. In addition, further uncontraction of the outermost region of the ANO basis set does not affect  $\alpha$ . The best value of  $\alpha$  obtained at the CCSD(T) level of theory is 11.21 a.u. The value becomes 11.17 a.u. when corrected for a core correlation contribution of  $-0.04$  a.u. (obtained using either the CCSD or MP2 method). The MP2 and CCSD results are within 1% of the CCSD(T) value indicating that  $\alpha$  is little affected by higher-order correlation effects. Basis set incompleteness and errors in the correlation treatment are unlikely to exceed 0.03 a.u.; the core correlation treatment, however, is probably much further from complete than the valence treatment, although the agreement between the MP2 and CCSD estimates is encouraging. We conservatively assign an uncertainty of 0.02 a.u. to this contribution, and arrive at a best estimated  $\alpha$  of  $11.17 \pm 0.05$  a.u., in good agreement with the MP4(SDTQ) value of 11.23 a.u. obtained by Cernusak, Diercksen and Sadlej<sup>17</sup> in calculations where the  $L$  shell was included in the determination of the correlation energy. These values compare well with the experimental result of 11.07 a.u. of Hohm and Kerl<sup>18</sup> and the value of 11.08 a.u. derived from dipole oscillator strength distributions (DOSD) by Kumar and Meath.<sup>19</sup>

The second hyperpolarizability,  $\gamma$ , is somewhat more sensitive to extension of the



one-particle basis set at the correlated level of theory. However, once the ANO basis set has been uncontracted to  $[5+1+1+1+1s\ 4+1+1+1p\ 2+1+1+1d\ 1+1+1f]$  further basis set saturation has little effect on  $\gamma$  at the CCSD level of theory. As we noted above, diffuse  $g$  functions increase  $\gamma$  only slightly. Using the CCSD(T)  $\gamma$  values from the various basis sets in Table 1, and assuming additivity of the triple excitation and basis set extension contributions, we arrive at our best valence-correlated estimate of 1234 a.u. for  $\gamma$ . This value is uncertain by about 5 a.u. because of the lack of  $g$  and higher angular momentum functions, by 6 a.u. because of the uncertainties in fitting, and perhaps 5 a.u. from errors in the correlation treatment.

The core correlation contribution has been computed at the MP2 and CCSD levels. These approaches give rather different results — 5 *vs* 12 a.u., respectively — unlike the situation for  $\alpha$ . We use the CCSD value as the best estimate available of core correlation effects, but in view of the large difference between the CCSD and MP2 values we have assigned an uncertainty of 12 a.u., that is, the entire CCSD value, to the effects of core correlation. This gives a best estimate  $\gamma$  of  $1220 \pm 30$  a.u.: significantly larger than Shelton’s most recent experimental result of  $1167 \pm 6$  a.u.<sup>2</sup> The experimental “static” value,  $\gamma_0$ , is deduced from a fit of DC second harmonic generation (DC-SHG) measurements extrapolated to zero frequency. (Recently, Shelton has determined the hyperpolarizability of argon at two frequencies (1064 and 1319 nm) and revised his previous estimate of  $\gamma_0$  from  $1108^{20}$  to  $1167 \pm 6$  a.u.<sup>2</sup>) Based on our experience with neon<sup>3</sup>, we feel it is unlikely that improvements in the one-particle basis set and the  $n$ -particle treatment would account for all of the 4.5% discrepancy between theory and experiment. We therefore believe Shelton’s  $\gamma_0$  for argon is somewhat too low, or that at least the experimental uncertainties are too small.

It is interesting to note that the MP2  $\gamma$  value of 1220 a.u. obtained with the  $[5+1+1s\ 4+1+1p\ 2+1+1d\ 1+1f] + (3s\ 3p\ 2d\ 3f)$  basis is close to the CCSD(T) result (1243 a.u.) while the CCSD result is lower, at 1177 a.u. There thus appears to be some cancellation between the infinite-order contributions of single and double excitations and the contribution from connected triple excitations estimated through perturbation theory in the CCSD(T) method. The MP2 value for  $\gamma$  including core correlation effects, 1209 a.u., may be compared with the MP2 value of 1272 a.u. determined by Cernusak and co-workers.<sup>17</sup> Given that our SCF value is 24 a.u. smaller than that of Ref. 17, a

difference that must be due entirely to basis set effects, it is not surprising that there is an even larger difference between the MP2 values. Similarly, the MP4(SDTQ) result for  $\gamma$  (1329 a.u.)<sup>17</sup> is higher than the 1219 a.u. value obtained by correcting our best CCSD(T) result by the CCSD estimate of core correlation, although these approaches are less comparable.

## B. Krypton and Xenon

The polarizabilities of krypton and xenon are reported in Tables 2 and 3, respectively. Our SCF dipole polarizability for krypton is 16.47 a.u. This is in good agreement with the value of 16.46 a.u. by McEachran et al.<sup>15</sup>, evaluated using a frozen-core coupled-perturbed Hartree-Fock (CPHF) approximation, even though our approach allows full relaxation of the core orbitals in the presence of the field. Our result is also very close to the value of 16.44 a.u. reported by Maroulis and Thakkar.<sup>21</sup> Comparison of the SCF  $\alpha$  values in Table 2 obtained with the various basis sets demonstrates that our result is converged with respect to addition of diffuse polarization functions and with respect to uncontraction of the ANO basis set. Electron correlation has a small effect, increasing  $\alpha$  by 4%. The MP2 (17.07 a.u.) and CCSD (17.03 a.u.) values are close to the MP2 (17.12 a.u.) and MP4(SDQ) (17.08 a.u.) values reported by Maroulis and Thakkar.<sup>21</sup> Connected triple excitations, as estimated by the CCSD(T) method, increase  $\alpha$  by less than 1%, yielding a best valence CCSD(T) value of 17.16 a.u. This is higher than the variation-perturbation configuration-interaction (VPCI) value of 16.79 a.u. of Hibbert and co-workers.<sup>22</sup> Core correlation decreases  $\alpha$  by 0.17 a.u. (or 1%) based on MP2 calculations. The final correction considered in this work is for relativistic effects. The relativistic correction to the polarizabilities is expected to be small, since these properties tend to be sensitive to the description of the outermost regions of the wave function. The correction obtained from the mass-velocity and Darwin terms, using first-order perturbation theory and SCF wave functions, is  $-0.08$  a.u. This can be compared with a correction of  $+0.01$  a.u. obtained from the difference between the relativistic random phase approximation (RRPA) calculations of Kolb and co-workers<sup>23</sup> and the CPHF values of McEachran et al.,<sup>15</sup> or a zero relativistic contribution by comparing our own non-relativistic SCF result to that of Ref. 23. The RRPA approach can be regarded as a “coupled-perturbed Dirac-Fock” treatment, and would reduce to CPHF in the non-relativistic limit. The results obtained with both these methods indicate that, as anticipated, the relativistic correction to  $\alpha$

is small ( $<1\%$ ), although the agreement between the RRPA contribution and the first-order perturbation theory estimate is rather poor. We use zero as an estimate of the relativistic contribution, but with an uncertainty of 0.08 a.u. Our best final estimate of the dipole polarizability  $\alpha$  for krypton is then  $17.16 - 0.17 + 0.00 = 17.0 \pm 0.2$  a.u. which is in good agreement with the DOSD derived value of 16.79 a.u. of Kumar and Meath.<sup>19</sup> In addition to the uncertainty in the relativistic correction, we include a contribution from core correlation, since our computed result of 0.17 a.u. is likely to increase somewhat with a more elaborate treatment.

The first dipole polarizability  $\alpha$  of xenon is determined to be 27.08 a.u. at the SCF level of theory with the  $[7+1+1s\ 6+1+1p\ 4+1+1d\ 1+1f] + (3s\ 3p\ 3d\ 3f)$  basis set, as shown in Table 3. This value changes by only 0.5% as the basis set is extended, and is close to the frozen-core CPHF value of 27.06 a.u.<sup>15</sup>, and within 0.1 a.u. of the value reported by Maroulis and Thakkar.<sup>21</sup> Considering only the valence shell, electron correlation increases  $\alpha$  by 3.3%; a smaller relative increase than for krypton. This follows the general trend of smaller correlation contributions to the polarizabilities as one goes down the periodic table. The MP2 (27.85 a.u.) and CCSD (27.84 a.u.) values are within 0.1 a.u. of the MP2 (27.77 a.u.) and MP4(SDQ) (27.76 a.u.) results of Maroulis and Thakkar,<sup>21</sup> and also the VPCI result (27.78 a.u.).<sup>22</sup> From comparison of our best CCSD(T) and CCSD results we see that connected triple excitations increase  $\alpha$  by only 0.15 a.u., hence higher excitations also become less important as we move to the heavier noble gases. The core correlation correction to  $\alpha$  is larger than for krypton, consistent with expectations that core-valence correlation contributions will increase in magnitude with increasing atomic number. These contributions reduce  $\alpha$  by 0.46 a.u., thereby reducing the total electron correlation contribution to  $\alpha$  to around 2%. Ignoring relativistic effects and assuming additivity of the correlation contributions gives an  $\alpha$  of 27.53 a.u., which is somewhat lower than previously reported values, although core correlation has not been considered in previous studies. The relativistic correction of  $-0.59$  a.u., determined from first-order perturbation theory, is considerably larger than the value of  $-0.13$  a.u. obtained from comparison of the RRPA value of Kolb and co-workers<sup>23</sup> with our non-relativistic SCF value. It thus appears that first-order perturbation theory may overestimate the relativistic effect on the Xe polarizability. Taking a relativistic correction of  $-0.13$  a.u. gives a best estimate for the polarizability  $\alpha$  of xenon of 27.4 a.u. Our

estimated uncertainty in this value will derive almost entirely from the core correlation and relativistic contributions; uncertainties of 0.3 a.u. in the former and 0.5 in the latter (which would then encompass both estimates of the relativistic correction) give us a final value of  $27.4 \pm 0.8$  a.u. This result is in good agreement with the DOSD value of 27.16 a.u. determined by Kumar and Meath.<sup>19</sup>

Theoretical calculations of the second hyperpolarizabilities for krypton and xenon have not been reported previously. For krypton,  $\gamma$  is determined to be 2260 a.u. at the SCF level of theory with a basis set of comparable quality to that used for argon. This value is insensitive to addition of diffuse  $g$  functions. Valence-shell electron correlation increases  $\gamma$  by 20%. Core correlation effects, as determined at the MP2 level of theory, reduce the total electron correlation contribution to 19%. Two one-particle basis sets were used in the determination of the correction due to core correlation. A tight  $f$  function was added to the second basis in order to test the need for additional core-correlating functions. Since there is no difference between the two MP2  $\gamma$  values, these basis sets seem adequate for core correlation. The relativistic correction determined using the mass-velocity and Darwin operators reduces  $\gamma$  by less than 1%, indicating that relativistic contributions to the hyperpolarizability of krypton may be neglected, just as for  $\alpha$ . Thus our best estimate for the second hyperpolarizability  $\gamma$  of krypton is  $2810 \pm 90$  a.u., with the largest uncertainty contribution (40 a.u.) arising from a possible underestimation of the core correlation contribution, as for argon. We estimate that incompleteness of the valence correlation treatment and the relativistic contribution contribute about 30 a.u. to the uncertainty and basis set incompleteness at most 20 a.u. Our  $\gamma$  value is somewhat higher than the experimentally derived value for  $\gamma_0$  of 2600 a.u.<sup>2</sup>

For xenon, the SCF value of 5870 a.u. for the second hyperpolarizability  $\gamma$  appears to be converged with respect to extension of the one-particle basis set. The addition of diffuse  $g$  functions to the one-particle basis set causes an increase of 70 a.u. or 1% to the CCSD(T) value of  $\gamma$ . The effect of electron correlation, considering both the valence shell and (additively) the MP2 core correlation correction, is to increase  $\gamma$  by 18%, a relative correction similar to that found for krypton. It is encouraging that for both krypton and xenon the MP2 estimate of the valence electron correlation is reliable, yielding a  $\gamma$  value between the CCSD and CCSD(T) results. Assuming additivity of one-particle basis set effects, we obtain 7030 a.u. for the second hyperpolarizability of xenon, excluding

relativistic effects. The perturbation theory estimate of relativistic effects reduces  $\gamma$  by only 10 a.u. or less than 0.5%. This is much smaller than the correction found for the first dipole polarizability  $\alpha$ , as may be expected since  $\gamma$  is a higher-order property less likely to be affected by the description of the core. Even if first-order perturbation theory greatly overestimates the relativistic contribution to  $\gamma$ , the effect on our final result would be small. Assuming once again that the MP2 estimate of core correlation may be in error by almost 100%, as for argon, and assuming an uncertainty of 60 a.u. for residual errors in the valence correlation treatment, basis set, and relativistic contribution, our predicted  $\gamma$  for xenon is  $7020 \pm 200$  a.u. This value is in rather good agreement with the experimental value for  $\gamma_0$  of 6888 a.u.<sup>2</sup>

### C. Neon and Helium

Table 4 summarizes our previous results for neon<sup>3</sup> obtained with basis sets comparable to those used for the heavier atoms in this work. The best estimates of  $\alpha$  and  $\gamma$  are  $2.69 \pm 0.03$  a.u. and  $119 \pm 4$  a.u., respectively. As noted previously,<sup>3</sup> these results are in good agreement with the CCD+ST(CCD) values of 2.70 ( $\alpha$ ) and 113.9 ( $\gamma$ ) a.u. of Maroulis and Thakkar<sup>24</sup> and compare very well with the experimental value of Kumar and Meath for  $\alpha$  (2.669 a.u.) and with the experimental result of Shelton for  $\gamma_0$  ( $119 \pm 2$  a.u.)<sup>2</sup>. The MP2 value of  $\gamma$  obtained with the  $[4+1+1s\ 3+1+1p\ 2+1+1d\ 1+1f] + (3s3p2d2f)$  basis set is also included for comparison. As with the situation for argon, the MP2 value is close to the final estimate and lies between the CCSD and CCSD(T) values.

We have also determined the second hyperpolarizability  $\gamma$  of helium with the theoretical methods used here, since the experimental values for neon and argon are determined relative to that for helium. Moreover, it is useful to compare these with the very accurate theoretical values of Bishop and Pipin<sup>25</sup>, these being the ones used by Shelton<sup>2</sup> in the evaluation of  $\gamma_0$  for neon and argon. Our results for the polarizabilities of helium are presented in Table 5.

There is excellent agreement for the dipole polarizability  $\alpha$  of helium between our CCSD result (note that CCSD is equivalent to full CI for a two-electron problem) and those of Bishop and Pipin<sup>25</sup> and Thakkar.<sup>26</sup> The CCSD value of 43.5 a.u. for  $\gamma$  of helium with a basis set including diffuse  $d$  polarization functions is little affected by including diffuse  $f$  functions in the one-particle basis set. This is consistent with the situation for neon, argon, krypton and xenon where diffuse  $g$  and higher angular momentum functions

affected  $\gamma$  by less than 1%. Our best estimate of  $\gamma$  for helium is 43.6 a.u. There is a small discrepancy of 0.5 a.u. or 1% between the CCSD result of  $\gamma$  for helium and the value of Bishop and Pipin (43.104 a.u.)<sup>25</sup> or Buckingham and Hibbard (43.10 a.u.).<sup>27</sup> However, this difference is not important here since the estimated error bars on our computed hyperpolarizabilities for the other noble gas atoms are larger than 1%.

Our MP2 value of  $\gamma$  for helium is in error by 6% compared with the CCSD value, which is a larger relative error than found for argon, krypton and xenon and is of the same magnitude as for neon. It is reasonable to expect that the MP2 level of theory should perform better for argon, krypton and xenon since the total electron correlation contribution to  $\gamma$  is around 20% whereas for neon the total electron correlation contribution is much larger at 40%. However, the electron correlation contribution to  $\gamma$  for helium is also around 20%. This underestimate of the electron correlation contribution at the MP2 level highlights the deficiencies of perturbation theory methods in describing a two-electron problem to a high degree of accuracy.

#### D. Ratios with respect to $\gamma_{He}$ or $\gamma_{Ar}$

Table 6 summarizes the comparison of our best results for all of the noble gas atoms with the appropriate experimental values. The ratios of  $\gamma$  for neon and argon relative to  $\gamma$  for helium, and  $\gamma$  for krypton and xenon relative to  $\gamma$  for argon are also presented, since it is actually these quantities that are derived from experiment.<sup>2</sup> Shelton's values of  $119 \pm 2$  a.u. for neon and  $1167 \pm 6$  a.u. for argon are determined relative to the value of 43.104 a.u. for helium from Bishop and Pipin's calculations<sup>25</sup>. Our ratio  $\gamma_{Ne} : \gamma_{He}$  is 2.73, or 2.76 using Bishop and Pipin's helium result. This is in excellent agreement with the experimental ratio extrapolated to zero frequency (accounting for an anomalous negative dispersion effect<sup>28</sup> for  $\gamma$  of neon). The ratios  $\gamma_{Ar} : \gamma_{He}$  determined theoretically and experimentally do not agree within the stated error bars. At the lowest frequency for which experimental measurements were made, the ratio  $\gamma_{Ar} : \gamma_{He}$  is  $27.84 \pm 0.16$ .<sup>2</sup> Extrapolation to zero frequency reduces this ratio by 3% to 27.07, whereas the theoretical value is 28.0. Using Bishop and Pipin's value of  $\gamma$  for helium results in little change in our ratio  $\gamma_{Ar} : \gamma_{He}$ , and the value is no closer to the experimental ratio.

The hyperpolarizabilities for krypton and xenon are experimentally determined from comparison with  $\gamma$  for argon. The difference between the theoretical (2.30) and experimental (2.23) values for  $\gamma_{Kr} : \gamma_{Ar}$  is smaller than the experimental value of  $\gamma_0$

for krypton would indicate, since comparing ratios effectively eliminates the discrepancy between theory and experiment for the hyperpolarizability of argon. In fact, a  $\gamma_{Kr} : \gamma_{Ar}$  ratio of 2.23 could be obtained theoretically if  $\gamma$  for krypton were 2720 a.u., a value that lies just within our uncertainty. Extrapolation of the experimental results to zero frequency would seem more reliable for the  $\gamma_{Kr} : \gamma_{Ar}$  ratio than for the  $\gamma_{Ar} : \gamma_{He}$  and  $\gamma_{Ne} : \gamma_{He}$  ratios, since  $\gamma_{Kr} : \gamma_{Ar}$  is reduced by only 0.01 relative to the lowest frequency measurement.

The experimental and theoretical ratios  $\gamma_{Xe} : \gamma_{Ar}$  agree somewhat better than was the case for krypton. Using the experimental  $\gamma_{Xe} : \gamma_{Ar}$  ratio together with our best theoretical estimate for  $\gamma$  of argon leads to a  $\gamma$  value for xenon that agrees better with our theoretical result than does the experimentally deduced value of Shelton.<sup>2</sup> For xenon, as for krypton, the experimental zero frequency ratio should be reliable since extrapolation to zero frequency reduces the ratio  $\gamma_{Xe} : \gamma_{Ar}$  only slightly. The major source of discrepancy between the theoretical and experimental hyperpolarizabilities for the heavier noble gases thus appears to be the argon hyperpolarizability used in conjunction with the experimental ratios.

#### 4. Conclusions

In this study, very accurate polarizabilities  $\alpha$  and  $\gamma$  of the noble gas atoms have been determined. The one-particle basis set requirements for description of the electric field response, in terms of the angular momentum quantum number, are essentially determined at the SCF level of theory, and our SCF values for these polarizabilities are close to the Hartree-Fock limit. We have taken account of electron correlation with the MP2, CCSD and CCSD(T) methods and our values at these levels of theory should be converged with respect to the one-particle basis set to within a few percent. As is expected, the effects of electron correlation in the valence shell are less important for the heavier atoms in the series since the atoms are larger and the region of space occupied by the valence electrons is greater. For example, neon shows the largest correlation contribution to  $\gamma$  (40%) compared to argon (23%), krypton (20%) and xenon (18%). Not surprisingly, the importance of core-valence correlation increases with increasing atomic number, but even for xenon this effect is only of the order of a few percent. We have also examined relativistic effects on the polarizabilities of the heavier atoms. The perturbation theory estimate used in this work, as well as the RRPA calculations of Kolb and co-workers,<sup>23</sup> indicates that these effects are negligible on the polarizabilities of krypton. Relativistic effects for the polarizabilities of xenon, particularly for  $\alpha$ , are larger in magnitude, and the perturbation theory correction seems less reliable.

In the light of the above discussion, the polarizabilities of argon should be more accurate than those for neon since electron correlation is easier to describe in argon. The  $\alpha$  and  $\gamma$  values for krypton, although necessarily including more corrections (core correlation and relativistic), should also be accurate since the contribution of these effects is small. In terms of absolute magnitude, the polarizabilities for xenon are more difficult to determine since both core correlation and relativistic effects are more important and this is reflected in the larger error bars for the polarizabilities of this atom. However, since the absolute magnitude of the hyperpolarizability  $\gamma$  is substantially larger for xenon than for the other noble gas atoms, the relative uncertainty in  $\gamma$  is similar. The dipole polarizability  $\alpha$  values determined in this work for neon, argon and krypton are in good agreement with the DOSD derived values of Kumar and Meath.<sup>19</sup> The value for xenon is not expected to be as reliable since we have assumed additivity of larger core correlation and relativistic corrections, although the agreement is encouraging. Given the exceptional



agreement between theory and experiment for the hyperpolarizability  $\gamma$  of neon, it is surprising that there is such poor agreement for  $\gamma$  of argon considering the accuracy of these calculations. There is also a considerable discrepancy for  $\gamma$  of krypton, which in part may be reduced by adjusting for the difference in the theoretical and experimental values for argon. The agreement between the theory and experiment for  $\gamma$  of xenon is reasonably good though the difference would be reduced if the experimental value for  $\gamma$  of argon were adjusted.

Finally, it is encouraging to note the small error associated with the MP2 method relative to the CCSD(T) approach when determining  $\gamma$  for argon (2%), krypton (2.5%) and xenon (3%). This indicates that the MP2 method may be useful for determining higher-order polarizabilities when the wave function is strongly dominated by a single determinant.

### Acknowledgements

PRT was supported by NASA Grant No. NCC 2-371. This work was partly supported by the National Science Foundation, grant CHE-8915629 (JA). Some of the calculations were performed using a grant of computer time from the NAS Facility.

## References

1. D.M. Bishop, Rev. Mod. Phys. **62**, 343 (1990).
2. D.P. Shelton, Phys. Rev. A **42**, 2578 (1990).
3. P.R. Taylor, T.J. Lee, J.E. Rice and J. Almlöf, Chem. Phys. Lett. **163**, 359 (1989).
4. K. Raghavachari, G.W. Trucks, J.A. Pople and M. Head-Gordon, Chem. Phys. Lett. **157**, 479 (1989).
5. J. Almlöf and P.R. Taylor, J. Chem. Phys. **86**, 4070 (1987).
6. A.D. Buckingham, Adv. Chem. Phys. **12**, 107 (1967).
7. F.B. van Duijneveldt, IBM Research Report RJ 945 (IBM, San Jose, 1971).
8. H. Partridge, J. Chem. Phys. **87**, 6643 (1987).
9. H. Partridge, J. Chem. Phys. **90**, 1043 (1989).
10. H. Partridge and K. Fægri, to be published.
11. R.D. Cowan and D.C. Griffin, J. Opt. Soc. Am. **66**, 1010 (1976); R.L. Martin, J. Phys. Chem. **87**, 750 (1983).
12. MOLECULE-SWEDEN is an electronic structure program system written by J. Almlöf, C.W. Bauschlicher Jr., M.R.A. Blomberg, D.P. Chong, A. Heiberg, S.R. Langhoff, P.-A. Malmqvist, A.P. Rendell, B.O. Roos, P.E.M. Siegbahn, and P.R. Taylor.
13. R.D. Amos and J.E. Rice, CADPAC: Cambridge Analytic Derivatives Package, Issue 4.0 (Cambridge University, Cambridge, England, 1987).
14. T.J. Lee and J.E. Rice, Chem. Phys. Lett. **150**, 406 (1988).
15. R.P. McEachran, A.D. Stauffer and S. Greita, J. Phys. B **12**, 3119 (1979).
16. R.E. Sitter and R.P. Hurst, Phys. Rev. A **5**, 5 (1972).
17. I. Cernusak, G.H.F. Dierksen and A. Sadlej, Chem. Phys. Lett. **128**, 18 (1986).
18. U. Hohm and K. Kerl, Mol. Phys., **69**, 819 (1990)
19. A. Kumar and W.J. Meath, Can. J. Chem., **63**, 1616 (1985).
20. V. Mizrahi and D.P. Shelton, Phys. Rev. Lett., **55**, 696 (1985).
21. G. Maroulis and A.J. Thakkar, J. Chem. Phys. **89**, 7320 (1988).
22. A. Hibbert, K.L. Bell and K.A. Berrington, J. Phys. B **20**, L349 (1987).
23. D. Kolb, W.R. Johnson and P. Shorer, Phys. Rev. A **26**, 19 (1982).
24. G. Maroulis and A.J. Thakkar, Chem. Phys. Lett. **156**, 87 (1989).

25. D.M. Bishop and J. Pipin, J. Chem. Phys. **91**, 3549 (1989).
26. A.J. Thakkar, J. Chem. Phys. **75**, 4496 (1981).
27. A.D. Buckingham and P.G. Hibbard, Symp. Faraday Soc., **2**, 41 (1968).
28. D.P. Shelton and Z. Lu, Phys. Rev. A **37**, 3813 (1988).
29. A.D. Buckingham and D.A. Dunmur, Trans. Faraday Soc. **64**, 1987 (1968).

**Table 1**  
Dipole polarizability,  $\alpha$ , and  
second hyperpolarizability,  $\gamma$ ,  
of argon (in a.u.).

Basis	Method	$\alpha$	$\gamma$
$A^a+(3s3p2d3f)$	SCF	10.73	967
$A+(3s3p2d3f)$	MP2	11.19	1220
$A+(3s3p2d3f)$	CCSD	11.10	1177
$A+(3s3p2d3f)$	CCSD(T)	11.20	1243
$A+(3s3p2d3f2g)$	SCF	10.73	967
$A+(3s3p2d3f2g)$	CCSD	11.11	1180
$A+(3s3p2d3f2g)$	CCSD(T)	11.21	1248
$B^b+(3s3p2d3f)$	SCF	10.75	965
$B+(3s3p2d3f)$	CCSD	11.11	1166
$B+(3s3p2d3f)$	CCSD(T)	11.21	1231
$C^c+(3s3p2d3f)$	SCF	10.76	966
$C+(3s3p2d3f)$	MP2	11.20	1214
$C+(3s3p2d3f)$	CCSD	11.12	1164
16 electrons correlated			
$C+(3s3p2d3f)$	MP2	11.16	1209
$C+(3s3p2d3f)$	CCSD	11.08	1152

<sup>a</sup> [ 5+1+1s 4+1+1p 2+1+1d 1+1f ] ANO basis.

<sup>b</sup> [ 5+1+1+1s 4+1+1+1p 2+1+1+1d 1+1+1f ] ANO basis.

<sup>c</sup> [ 11s 9p 8d 4f ] ANO basis.

**Table 2**  
Dipole polarizability,  $\alpha$ , and  
second hyperpolarizability,  $\gamma$ , of krypton (in a.u.).

Basis	Method	$\alpha$	$\gamma$
$A^a+(3s3p3d3f)$	SCF	16.47	2260
$A+(3s3p3d3f)$	MP2	17.07	2740
$A+(3s3p3d3f)$	CCSD	17.01	2680
$A+(3s3p3d3f)$	CCSD(T)	17.14	2810
$A+(3s3p3d3f3g)$	SCF	16.47	2260
$A+(3s3p3d3f3g)$	CCSD	17.03	2700
$A+(3s3p3d3f3g)$	CCSD(T)	17.16	2830
$B^b+(3s3p3d3f)$	SCF	16.47	2260
$B+(3s3p3d3f)$	MP2	17.07	2740
$C^c+(3s3p3d3f)$	SCF	16.47	2260
$C+(3s3p3d3f)$	MP2	17.07	2740
26 electrons correlated			
$B+(3s3p3d3f)$	MP2	16.89	2700
$C+(3s3p3d3f)$	MP2	16.90	2700
Relativistic correction			
$A+(3s3p3d3f)$	SCF	16.39	2280

<sup>a</sup> [ 6+1+1s 5+1+1p 3+1+1d 1+1f ] ANO basis.

<sup>b</sup> [ 6+1+1s 5+1+1p 3+1+1d 3+1f ] ANO basis.

<sup>c</sup> [ 6+1+1s 5+1+1p 3+1+1d 4+1f ] ANO basis.

**Table 3**  
Dipole polarizability,  $\alpha$ , and  
second hyperpolarizability,  $\gamma$ , of xenon (in a.u.).

Basis	Method	$\alpha$	$\gamma$
$A^a+(3s3p3d3f)$	SCF	27.08	5870
$A+(3s3p3d3f)$	MP2	27.85	6900
$A+(3s3p3d3f)$	CCSD	27.82	6830
$A+(3s3p3d3f)$	CCSD(T)	27.99	7110
$A+(3s3p3d3f3g)$	SCF	27.08	5870
$A+(3s3p3d3f3g)$	CCSD	27.84	6880
$A+(3s3p3d3f3g)$	CCSD(T)	27.99	7180
$B^b+(3s3p3d3f)$	SCF	27.10	5870
$B+(3s3p3d3f)$	MP2	27.86	6890
26 electrons correlated			
$B+(3s3p3d3f)$	MP2	27.40	6750
Relativistic correction			
$A+(3s3p3d3f)$	SCF	26.49	5860

<sup>a</sup> [ 7+1+1s 6+1+1p 4+1+1d 1+1f ] ANO basis.

<sup>b</sup> [ 7+1+1s 6+1+1p 4+1+1d 4+1f ] ANO basis.

**Table 4**  
Dipole polarizability,  $\alpha$ , and  
second hyperpolarizability,  $\gamma$ ,  
of neon (in a.u.)<sup>a</sup>.

Basis	Method	$\alpha$	$\gamma$
$A^b+(3s3p2d3f)$	SCF	2.34	71.9
$A+(3s3p2d3f)$	CCSD	2.61	107.3
$A+(3s3p2d3f2g)$	SCF	2.34	72.2
$A+(3s3p2d3f2g)$	CCSD	2.61	108.1
$B^c+(3s3p2d3f)$	SCF	2.38	71.2
$B+(3s3p2d3f)$	MP2	2.71	110.8
$B+(3s3p2d3f)$	CCSD	2.64	108.7
$B+(3s3p2d3f)$	CCSD(T)	2.69	118.3
$C^d+(3s3p2d3f)$	CCSD	2.64	108.1
10 electrons correlated			
$C+(3s3p2d3f)$	CCSD	2.63	107.6

<sup>a</sup> Taken from Ref. 3 (MP2 result is from this work).

<sup>b</sup> [ 4+1s 3+1p 2+1d 1+1f ] ANO basis.

<sup>c</sup> [ 4+1+1s 3+1+1p 2+1+1d 1+1f ] ANO basis.

<sup>d</sup> [ 13s 8p 8d 4f ] uncontracted basis.

**Table 5**  
Dipole polarizability,  $\alpha$ , and  
second hyperpolarizability,  $\gamma$ ,  
of helium (in a.u.).

Basis	Method	$\alpha$	$\gamma$
$A^a + (3s2p2d)$	SCF	1.322	36.2
$A + (3s2p2d)$	MP2	1.359	40.6
$A + (3s2p2d)$	CCSD	1.383	43.5
$B^b + (3s2p2d2f)$	SCF	1.322	36.2
$B + (3s2p2d2f)$	MP2	1.361	40.8
$B + (3s2p2d2f)$	CCSD	1.384	43.6

<sup>a</sup> [ 4+1+1s 3+1+1p 2+1d ] ANO basis.

<sup>b</sup> [ 4+1+1s 3+1+1p 2+1d 1+1f ] ANO basis.



**Table 6**

Best estimates of  $\alpha$  and  $\gamma$   
for the noble gases (in a.u.).

	$\alpha^a$ theory	$\alpha^b$ expt	$\gamma^a$ theory	$\gamma$ expt	$\gamma/\gamma_{He}$ theory	$\gamma/\gamma_{He}$ expt	$\gamma/\gamma_{Ar}$ theory	$\gamma/\gamma_{Ar}$ expt
He	1.384(1.383) <sup>c</sup>		43.6(43.104) <sup>c</sup>		-	-	-	-
Ne	2.63( $\pm 0.03$ )	2.669	119( $\pm 4$ )	119( $\pm 2$ ) <sup>d</sup> 101( $\pm 8$ ) <sup>f</sup>	2.73(2.76) <sup>e</sup>	2.76 2.34	-	-
Ar	11.2( $\pm 0.1$ )	11.08	1220( $\pm 30$ )	1167( $\pm 6$ ) <sup>d</sup> 1101( $\pm 8$ ) <sup>g</sup>	28.0(28.3) <sup>e</sup>	27.1 25.5	-	-
Kr	17.0( $\pm 0.2$ )	16.79	2810( $\pm 90$ )	2600 <sup>d</sup>	64.2(65.0) <sup>e</sup>	60.3	2.30	2.23
Xe	27.4( $\pm 0.5$ )	27.16	7030( $\pm 200$ )	6888 <sup>d</sup>	161(163) <sup>e</sup>	160	5.75	5.90

<sup>a</sup> Best estimates from this work, with uncertainties (see text).

<sup>b</sup> Kumar and Meath.<sup>19</sup>

<sup>c</sup> Bishop and Pipin.<sup>25</sup>

<sup>d</sup> Shelton.<sup>2</sup>

<sup>e</sup> The value in parentheses refers to the ratio relative to  $\gamma_{He}=43.104$ .

<sup>f</sup> Buckingham and Dunmur.<sup>29</sup>

<sup>g</sup> Mizrahi and Shelton.<sup>20</sup>